

Heats of Combustion and Isomerization of the Six C₇H₁₄ Alkylcyclopentanes

By Walter H. Johnson, Edward J. Prosen, and Frederick D. Rossini

The heats of isomerization of the six C₇H₁₄ alkylcyclopentanes were determined by measurement of the ratios of the heats of combustion of purified samples of these compounds in the liquid state by the procedure previously described for other isomeric hydrocarbons. The data yield the following values for the heat of isomerization, ΔH° , in the liquid state at 25° C, of ethylcyclopentane into each of the dimethylcyclopentanes, in kilocalories per mole: Ethylcyclopentane, 0.00; 1,1-dimethylcyclopentane, -2.06 ± 0.12 ; *cis*-1,2-dimethylcyclopentane, -0.44 ± 0.20 ; *trans*-1,2-dimethylcyclopentane, -1.86 ± 0.16 ; *cis*-1,3-dimethylcyclopentane, -1.11 ± 0.24 ; *trans*-1,3-dimethylcyclopentane, -1.60 ± 0.14 . These values were combined with values for the differences in the heats of vaporization of these isomers to obtain values for the heats of isomerization in the gaseous state at 25° C.

Utilizing the values previously reported for the heats of combustion and formation of ethylcyclopentane in the liquid and gaseous states at 25° C, values were calculated for the heats of combustion and formation of the five dimethylcyclopentanes in the liquid and gaseous states at 25° C.

I. Introduction

In continuation of the program of determining the heats of combustion, formation, and isomerization of hydrocarbons of various types [1],¹ calorimetric measurements have been made that yield values for the differences in the heats of combustion, or the heats of isomerization, of the six C₇H₁₄ alkylcyclopentanes in the liquid state at 25° C. These values of heats of isomerization were combined with values [2] for the differences in the heats of vaporization of these isomers at 25° C to obtain values for the heats of isomerization in the gaseous state at 25° C. Utilizing the values previously reported [3] for the heats of combustion and formation of ethylcyclopentane in the liquid and gaseous states at 25° C, corresponding values were calculated for the five dimethylcyclopentanes.

II. Unit of Energy, Molecular Weights, Uncertainties

The unit of energy upon which values reported in this paper are based is the absolute joule, derived from mean solar seconds and absolute ohms and volts, in terms of which certification of standard resistors and cells is made by this Bureau. For conversion to the conventional thermochemical calorie, the following relation is used [4, 5]:

$$1 \text{ calorie} = 4.1840 \text{ absolute joules.}$$

The molecular weight of carbon dioxide, the mass of which was used to determine the amount of reaction, was taken as 44.010, from the 1947 table of international atomic weights [6].

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method previously described [7].

¹ Figures in brackets indicate the literature references at the end of this paper.

Definitions of the symbols used are given in previous papers [1, 8].

III. Method and Apparatus

The same method and apparatus were used as in the investigations recently reported from this laboratory [1]. One calorimetric system, resistance bridge (No. 404), and platinum resistance thermometer (No. 373,730) were used for all the experiments reported here.

No products associated with incomplete combustion were found in any of the experiments.

IV. Materials

The compounds used in the present investigation were samples from the API-NBS series of highly purified hydrocarbons, which are being prepared through a cooperative undertaking of the American Petroleum Institute and the National Bureau of Standards.

These samples of API-NBS hydrocarbons have been made available by the American Petroleum Institute and the National Bureau of Standards through the API Research Project 44 on the "Collection, analysis, calculation, and compilation of data on the properties of hydrocarbons." The samples were purified at the National Bureau of Standards by the API Research Project 6 on the "Analysis, purification, and properties of hydrocarbons," from material supplied by the following laboratories:

Ethylcyclopentane (A), *cis*-1,3-dimethylcyclopentane, and *trans*-1,3-dimethylcyclopentane (A) by the American Petroleum Institute Research Project 45 at the Ohio State University, Columbus, Ohio, under the supervision of C. E. Boord.

1,1-Dimethylcyclopentane, *cis*-1,2-dimethylcyclopentane, and *trans*-1,2-dimethylcyclopentane by Hydrocarbon Laboratory at the Pennsylvania State College, State College, Pa.

A complete description of the purification, purity, and freezing points of the six API-NBS hydrocarbons used in the present investigation is given in references [9, 10, 11], which reported the amounts of impurity in these samples, as determined from measurements of freezing points, to be as follows in mole fraction: Ethylcyclopentane (A), 0.0008 \pm 0.0004; 1,1-dimethylcyclopentane, 0.0003 \pm 0.0002; *cis*-1,2-dimethylcyclopentane, 0.00025 \pm 0.00016; *trans*-1,2-dimethylcyclopentane, 0.0013 \pm 0.0010; *cis*-1,3-dimethylcyclopentane, 0.0041 \pm 0.0023; *trans*-1,3-dimethylcyclopentane (A) 0.0035 \pm 0.0009.

As the manner of purification [9, 10, 11] was such as to leave substantially only close-boiling isomeric impurities in the respective compounds, it is calculated that in the extreme case the measured heat of combustion would be affected by less than 0.001 percent because of impurities.

The samples of *trans*-1,2-dimethylcyclopentane and *trans*-1,3-dimethylcyclopentane are the *racemic* mixtures of the *dextro* and *levo* forms. With regard to energy content, the *dextro* and *levo* forms are identical, and any difference between these and the *racemic* mixture would be insignificant.

V. Results

The experimental results of the present investigation are summarized in table 1, which gives for each of the six compounds the following data: The number of experiments performed; the minimum and maximum values of the mass of carbon dioxide formed in the combustion and of the calorimetric quantities, ΔR_c , Δr_i , and Δr_n [8]; the mean value of B , and its standard deviation, in ohms per gram of carbon dioxide formed, as defined by eq 4 of reference [8]. The symbols have the same significance as in reference [1].

In table 2 are given, for the six C_7H_{14} alkylcyclopentanes, values of the following: The constant B , in ohms per gram of carbon dioxide, as given in table 1; B° , which is the value of B corrected to the ideal bomb reaction by the method of Washburn [12]²; B_i°/B_n° , which is equal to the ratio of the heat evolved, per mole of hydrocarbon, in the ideal bomb process at 28° C for each isomer to that of ethylcyclopentane; and $(-\Delta U^\circ)_n - (-\Delta U^\circ)_i$, the difference, between ethylcyclopentane and each isomer, in the heat of combustion in the ideal bomb process at 28° C.

² The Washburn correction is the same for all these compounds as they are isomers, but account is taken of the variation of the correction with the amount of sample burned. As used here, the Washburn correction was modified to apply to 28° C (the temperature to which the measured heat of combustion is referred) and to the gases at zero pressure (instead of 1 atmosphere).

TABLE 1. Results of the calorimetric combustion experiments

| Compound | Number of experiments | Mass of carbon dioxide formed | ΔP_c | Δr_i | Δr_n | B | |
|---|-----------------------|-------------------------------|----------------------------|----------------------------|----------------------------|-----------------------------|-----------------------------|
| | | | | | | Mean | Standard deviation of mean |
| | | <i>g</i> | <i>Ohm</i> | <i>Ohm</i> | <i>Ohm</i> | <i>Ohm/g CO₂</i> | <i>Ohm/g CO₂</i> |
| Ethylcyclopentane..... | 7 | 2.69117 to 2.86858 | 0.293466 to 0.312878 | 0.000254 to 0.000263 | 0.000004 to 0.000005 | 0.1089810 | ±0.000055 |
| 1,1-Dimethylcyclopentane..... | 5 | 2.61833 to 2.82697 | 0.285029 to 0.307731 | 0.000253 to 0.000262 | 0.000003 to 0.000003 | | |
| <i>cis</i> -1,2-Dimethylcyclopentane..... | 7 | 2.76937 to 2.87510 | 0.301970 to 0.313576 | 0.000240 to 0.000259 | 0.000056 to 0.000066 | .1089371 | ±.000085 |
| <i>trans</i> -1,2-Dimethylcyclopentane..... | 7 | 2.68335 to 2.86133 | 0.292203 to 0.311521 | 0.000253 to 0.000263 | 0.000006 to 0.000065 | | |
| <i>cis</i> -1,3-Dimethylcyclopentane..... | 5 | 2.46454 to 2.69782 | 0.268433 to 0.293898 | 0.000259 to 0.000271 | 0.000065 to 0.000075 | .1088694 | ±.0000106 |
| <i>trans</i> -1,3-Dimethylcyclopentane..... | 5 | 2.73538 to 2.81293 | 0.297897 to 0.306325 | 0.000253 to 0.000255 | 0.000006 to 0.000006 | | |

TABLE 2. Heats of isomerization in the liquid state

| Compound | B at 28° C | B° at 28° C | Ratio of the heats of combustion in the ideal bomb process, B_i^0/B_n^0 , at 28.00° C | Difference in the heats of combustion in the ideal bomb process, $(-\Delta U^0)_n - (-\Delta U^0)_i$, at 28.00° C | |
|---|--------------------|--------------------|---|--|------------------|
| | | | | <i>kJ/mole</i> | <i>kcal/mole</i> |
| Ethylcyclopentane..... | 0.1089810±.0000110 | 0.1089503±.0000108 | 1.000000 | 0.00 | 0.00 |
| 1,1-Dimethylcyclopentane..... | .1087759±.0000064 | .1087453±.0000062 | 0.998118±.000114 | 8.62±0.52 | 2.06±.12 |
| <i>cis</i> -1,2-Dimethylcyclopentane..... | .1089371±.0000170 | .1089063±.0000170 | .999596±.000185 | 1.85±0.85 | 0.44±.20 |
| <i>trans</i> -1,2-Dimethylcyclopentane..... | .1087961±.0000116 | .1087655±.0000116 | .998304±.000146 | 7.77±0.67 | 1.86±.16 |
| <i>cis</i> -1,3-Dimethylcyclopentane..... | .1088694±.0000212 | .1088394±.0000212 | .998982±.000219 | 4.66±1.00 | 1.11±.24 |
| <i>trans</i> -1,3-Dimethylcyclopentane..... | .1088215±.0000090 | .1087908±.0000090 | .998536±.000129 | 6.71±0.59 | 1.60±.14 |

The values of the differences in the heats of combustion in the ideal bomb process, $(-\Delta U^0)_n - (-\Delta U^0)_i$, were obtained by means of the relation [8]

$$(-\Delta U^0)_n - (-\Delta U^0)_i = (-\Delta U^0)_n \left(1 - \frac{B_i^0}{B_n^0}\right).$$

For this calculation, the value of $(-\Delta U^0)_n$ at 28°C was taken from reference [13] as 4581.5 int kj/mole or 4582.3 abs kj/mole.

In table 3 are given, for the six C_7H_{14} alkylcyclopentanes, values for the following: $H_i^0 - H_n^0$,

the heat of isomerization of ethylcyclopentane into each isomer at 25° C for the liquid and gaseous states; $-\Delta Hc^0$, the decrement in the heat content accompanying the reaction of combustion of the hydrocarbon in the liquid or gaseous state, as indicated, in gaseous oxygen to form gaseous carbon dioxide and liquid water at 25° C; and ΔHf^0 , the increment in heat content or enthalpy of the process of forming the given hydrocarbon in the liquid or gaseous state, as indicated, from its elements, gaseous hydrogen and solid carbon (graphite), at 25° C.

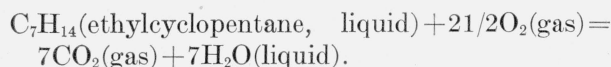
TABLE 3. Heats of isomerization, combustion, and formation in the liquid and gaseous states

| Compound | Heat of isomerization, $H_i^\circ - H_n^\circ$, at 25° C | | Heat of combustion, $-\Delta H_c^\circ$, at 25° C | | Heat of formation, ΔH_f° , at 25° C | |
|---|---|--------------------------|--|---------------------------------|--|--------------------------------|
| | Liquid | Gas | Liquid | Gas | Liquid | Gas |
| Ethylcyclopentane..... | <i>kcal/mole</i> 0.00 | <i>kcal/mole</i> 0.00 | <i>kcal/mole</i> 1097.50±.22 | <i>kcal/mole</i> 1106.23±.23 | <i>kcal/mole</i> -39.08±.24 | <i>kcal/mole</i> -30.35±.25 |
| 1,1-Dimethylcyclopentane..... | -2.06±.12 | -2.70±.12 | 1095.44±.25 | 1103.53±.26 | -41.14±.27 | -33.05±.28 |
| <i>cis</i> -1,2-Dimethylcyclopentane..... | -0.44±.20 | -0.61±.20 | 1097.06±.30 | 1105.62±.30 | -39.52±.31 | -30.96±.32 |
| <i>trans</i> -1,2-Dimethylcyclopentane..... | -1.86±.16 | -2.32±.16 | 1095.64±.27 | 1103.91±.28 | -40.94±.29 | -32.67±.30 |
| <i>cis</i> -1,3-Dimethylcyclopentane..... | -1.11±.24 | -1.58±.24 | 1096.39±.33 | 1104.65±.33 | -40.19±.34 | -31.93±.35 |
| <i>trans</i> -1,3-Dimethylcyclopentane..... | -1.60±.14 | -2.12±.14 | 1095.90±.26 | 1104.11±.27 | -40.68±.28 | -32.47±.29 |

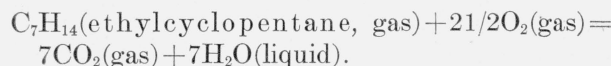
The heat of isomerization, $H_i^\circ - H_n^\circ$, in the liquid state at 25° C was taken as equal to the difference $(-\Delta U^\circ)_i - (-\Delta U^\circ)_n$ between each isomer and ethylcyclopentane, in the heats of combustion in the ideal bomb process at 28° C, since for these isomers the conversion to the constant-pressure process and to 25° C will be the same, well within the limits of uncertainty assigned to the values.

The heats of isomerization, $H_i^\circ - H_n^\circ$, in the gaseous state, were obtained from the values in the liquid state by use of the following values for the difference in the heat of vaporization of each isomer to that of ethylcyclopentane [2], in kcal/mole: Ethylcyclopentane, 0.00; 1,1-dimethylcyclopentane, 0.64; *cis*-1,2-dimethylcyclopentane, 0.17; *trans*-1,2-dimethylcyclopentane, 0.46; *cis*-1,3-dimethylcyclopentane, 0.47; *trans*-1,3-dimethylcyclopentane, 0.52.

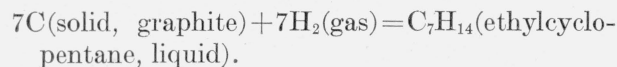
The value of the heat of combustion or formation of a given isomer was obtained by appropriately combining the heat of isomerization with the heat of combustion or formation of ethylcyclopentane as given by the following values from references [13, 14, 15]:



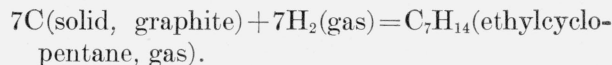
$$\Delta H_{298.16}^\circ = -1097.50 \pm 0.22 \text{ kcal/mole.}$$



$$\Delta H_{298.16}^\circ = -1106.23 \pm 0.23 \text{ kcal/mole.}$$



$$\Delta H_{298.16}^\circ = -39.08 \pm 0.24 \text{ kcal/mole.}$$



$$\Delta H_{298.16}^\circ = -30.35 \pm 0.25 \text{ kcal/mole.}$$

All the uncertainties assigned to the experimental quantities in table 2 (except the heats of combustion and formation) are equal to twice the standard deviation of the mean. The uncertainties assigned to the values of the heats of combustion and formation were obtained by combining [7] the uncertainty in the values of the heats of combustion and formation of ethylcyclopentane [14], with the uncertainties in the values of the heats of isomerization. The uncertainty to be assigned to the value of the heat of isomerization of any one of the isomers into any other one may conservatively be taken as ± 0.25 kcal/mole.

VI. References

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- [15] Selected Values of Properties of Hydrocarbons. American Petroleum Institute Research Project 44 at the National Bureau of Standards. Table 6n. Cyclopentanes C₅ to C₇. Heat of Combustion at 25° C, for liquid and gas (October 31, 1948).

WASHINGTON, November 16, 1948.